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<p>(21) International Application Number: PCT/US79/00370 (22) International Filing Date: 30 May 1979 (30.05.79) (31) Priority Application Number: 911,919 (32) Priority Date: 2 June 1978 (02.06.78) (33) Priority Country: US (71) Applicant: GENERAL ELECTRIC COMPANY [US/US]; 1 River Road, Schenectady, NY 12345 (US). (72) Inventor: LEE, Gim, Fun, Jr.; 11 Drawbridge Drive, Albany, NY 12203 (US).</p>		<p>(74) Agents: KING, Arthur, M.; General Electric Company, 570 Lexington Avenue, New York, NY 10022 (US), et al. (81) Designated States: DE (European patent), FR (European patent), GB (European patent), JP. Published with: <i>International search report</i></p>
<p>(54) Title: COMPOSITIONS COMPRISING POLYPHENYLENE ETHER AND POLY(VINYL CHLORIDE) RESINS</p> <p>(57) Abstract</p> <p>There are provided thermoplastic compositions which comprise, in intimate admixture, (a) polyphenylene ether resin, a plasticizer for (a) in an amount at least sufficient to reduce the fusion temperature to below that at which degradation of component (c) (i) or (ii) occurs; and (c) (i) a poly(vinyl chloride) resin or (ii) a combination thereof with a plasticizer therefor, the degradation temperature of (c) (i) or (c) (ii) being at least as high as the fusion temperature of component (a) <i>per se</i>.</p>		

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DescriptionCompositions Comprising Polyphenylene
Ether and Poly (vinyl chloride) Resins

The present invention relates to plasticized
5 thermoplastic compositions of polyphenylene ether
resins and poly(vinyl chloride) resins. The
compositions of this invention possess good
mechanical properties after molding, indicating an
absence of significant degradation of the poly(vinyl
10 chloride) resin component during mixing.

Cross-reference to Related Application

This application is a continuation-in-part of
copending application, Serial No. 752,731, filed
December 21, 1976.

15 Background of the Art

The polyphenylene ether resins are well known
in the art as a class of thermoplastics which posses
a number of outstanding physical properties. They
can be prepared, in general, by oxidative and non-
20 oxidative methods, such as are disclosed, for
example, in Hay, U.S. 3,306,874 and 3,306,875 and
Stamatoff, U.S. 3,257,357 and 3,257,358, which are
incorporated herein by reference.

It is known that when the polyphenylene ether
25 resins are combined with styrene resins, such
as crystal grade homopolystyrene or high impact rubber



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modified polystyrene, there are obtained compositions having many properties which are improved over those of either the polyphenylene ether or polystyrene alone. Moreover, these respective polymers are combinable in virtually all proportions, e.g., from 1 to 99 parts of polyphenylene ether to 99 to 1 parts of polystyrene. Examples of polyphenylene ether-polystyrene compositions are disclosed in Cizek, U.S. 3,383,435, which is incorporated herein by reference.

It has been thought to be practically impossible, however, to combine polyphenylene ether resins with poly(vinyl chloride) resins because the high melting (fusion) point of the polyphenylene ethers coupled with the notoriously poor thermal stability of poly(vinyl chloride) resins makes attempts at fusion blending, e.g., by hot roll milling, intensive mixing, co-extrusion and the like, lead to severe molecular weight degradation, hydrogen chloride evolution, color development, and the like.

It has now been found possible to produce such blends if the polyphenylene ether is first combined with a plasticizer to reduce its fusion temperature to below that at which severe degradation of poly(vinyl chloride) takes place, and then to intimately admix the components, the poly(vinyl chloride) optionally containing a further amount of the same, or a different, plasticizer.

Compositions produced according to this invention are economically attractive, can have a wide degree of properties, and, depending in the amount



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of poly(vinyl chloride), they are quite resistant to open flames. They can be fabricated by any of the common techniques into various molded and shaped articles. They can also contain fillers, both reinforcing and non-reinforcing, and additional additives, such as flame retardants, colorants, pigments, stabilizers, impact improvers, e.g., acrylic-rubber graft copolymers, styrene-butadiene block copolymers, acrylonitrile-butadiene-styrene terpolymers, and the like. In preferred features, the compositions will also include polystyrene resins in combination with the polyphenylene ether resins, the former being of the type disclosed in above-mentioned U.S. 3,383,435.

15 Description of the Invention

According to the present invention there are provided thermoplastic compositions which comprise, in intimate admixture:

- (a) a polyphenylene ether resin;
- 20 (b) a plasticizer for component (a) in an amount at least sufficient to reduce the fusion temperature of (a) to below that at which degradation of component (c) (i) or (ii) occurs; and
- (c) (i) poly(vinyl chloride) resin or (ii) a
- 25 combination thereof with a plasticizer therefor, the degradation temperature of (c) (i) or (c) (ii) being at least as high as the fusion temperature of component (a) per se.

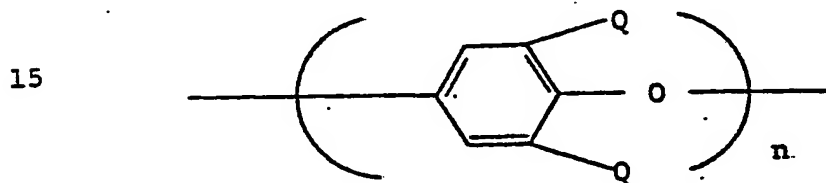
As employed herein the term "reduce the fusion
30 temperature" is used to describe compositions having a sufficient amount of a plasticizer which reduces



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the temperature required for extrusion of the polyphenylene ether per se by at least 50 to 100°F. as compared to the analagous unplasticized compositions. In practical terms, poly(2,6-dimethyl-1,4-phenylene) ether has a fusion temperature of above about (500°F.) 260°C per se. Enough plasticizer should be added to reduce the fusion temperature to below about (300°F) 149°C. Such a temperature is also below that at which severe degradation of poly(vinyl chloride) occurs, e.g., (350°F.) 177°C.

The polyphenylene ether resin (a) is preferably of the type having the structural formula:



20 wherein the oxygen ether atom of one unit is connected to the benzene nucleus of the next adjoining unit, n is a positive integer and is at least 50, and each Q is a monovalent substituent selected from the group consisting of hydrogen, halo-
 25 gen, hydrocarbon radicals free of a tertiary alpha-carbon atom, halohydrocarbon radicals having at least two carbon atoms between the halogen atom and the phenyl nucleus, hydrocarbonoxy radicals and halohydrocarbonoxy radicals having at least two
 30 carbon atoms between the halogen atom and the phenyl nucleus.

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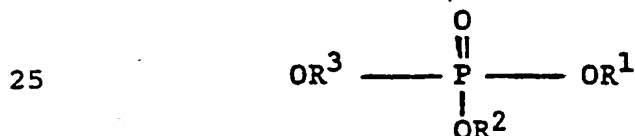
A more preferred class of polyphenylene ether resins for the compositions of this invention includes those of the above formula wherein each Q is alkyl, most preferably having from 1 to 4 carbon atoms.

- 5 Illustratively, members of this class include poly (2,6-dimethyl-1,4-phenylene)ether; poly(2,6-diethyl-1,4-phenylene)ether; poly(2-methyl-6-ethyl-1,4-phenylene)ether; poly(2-methyl-6-propyl-1,4-phenylene) ether; poly(2,6-dipropyl-1,4-phenylene)ether; poly
10 (2-ethyl-6-propyl-1,4-phenylene)ether; and the like.

Especially preferred is poly(2,6-dimethyl-1,4-phenylene)ether, preferably having an intrinsic viscosity of about 0.45 deciliters per gram (dl./g.) as measured in chloroform at 30°C.

- 15 The choice of plasticizer component (b) is not critical and any of the conventional materials used for this purpose can be employed. Preferably, component (b) will be selected from among phthalate and phosphate plasticizing materials, and especially
20 phosphate plasticizers.

The phosphate plasticizer is preferably a compound of the formula:



- wherein R¹, R² and R³ are the same or different and are alkyl, cycloalkyl, aryl, alkyl substituted aryl,
30 aryl substituted alkyl, hydroxyalkyl, hydroxyaryl, hydroxyalkaryl, halogen, haloaryl, and hydrogen.



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Examples include cresyl diphenyl phosphate, 2-ethylhexyl diphenyl phosphate, tricresyl phosphate, triisopropylphenyl phosphate, triphenyl phosphate, triethyl phosphate, dibutyl phenyl phosphate, 5 diethyl phosphate, cresyl diphenyl phosphate, isooctyl diphenyl phosphate, tributyl phosphate, 2-ethylhexyl diphenyl phosphate, isodecyl diphenyl phosphate, isodecyl dicresyl phosphate, didecyl cresyl phosphate, tri-n-hexyl phosphate, di-n-octyl 10 phenyl phosphate, di-2-ethyl-hexyl phenyl and tri-2-ethylhexyl phosphate tri(polychlorophenyl) phosphate or mixtures thereof. Especially preferred is triphenyl phosphate.

Examples of phthalate plasticizers include 15 dibenzyl phthalate, phenyl cresyl phthalate, diethyl phthalate, dimethyl phthalate, phenyl benzyl phthalate, butyl benzyl phthalate, butyl cyclohexyl phthalate, dibutyl phthalate, octyl cresyl phthalate, diphenyl phthalate, di-n-hexyl phthalate, 20 disohexyl phthalate, butyl octyl phthalate, butyl decyl phthalate, diisooctyl phthalate, di-2-ethyl-hexyl phthalate, di-n-octyl phthalate, diisononyl phthalate, diisodecyl phthalate, di-2-propyl heptyl phthalate, di-n-nonyl phthalate, di-n-decyl 25 phthalate ditridecyl phthalate and tris(2-ethylhexyl) tris(trimellitate).

The plasticizer (b) is added in amounts which will be sufficient to provide a plasticized composition within the meaning of the term described above. 30 In general, the plasticizer is present in amounts ranging from about 15 to about 65 parts of plasticizer per 100 parts of total resin. Preferably from about 20 to about 45 parts of plasticizer per 100 parts of total resin are employed.



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The vinyl polymer component (c) of the present compositions will comprise poly(vinyl chloride) and its copolymers. They will have a molecular weight of about 25,000 to 150,000. Minor amounts of 5 comonomers, e.g., vinylidene chloride vinyl acetate and the like can be present in polymerized form with vinyl chloride. All of the components (c) will be characteristically subject to high temperature degradation, releasing hydrogen chloride gas by 10 various decomposition mechanisms.

In embodiments of the invention, component (c) can further include (ii) a plasticizer. In general, any vinyl plasticizer can be employed, but those mentioned under (b) above are preferred. Especially 15 preferred is tris(2-ethylhexyl) trimellitate.

In general, the amounts of components (c) (i) or (c) (ii) will vary between 1 and 99 parts by weight to 99 to 1 part by weight of components (a) and (b), combined. Preferably the amounts of (c) (i) 20 or (c) (ii) will vary between 40 and 60 parts by weight per 60 to 40 parts by weight of components (a) and (b) combined.

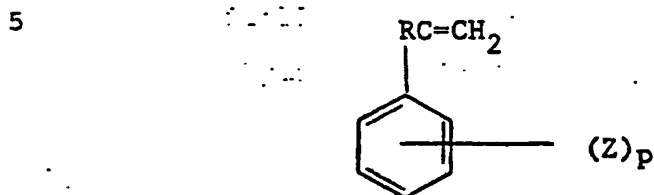
Conventional fillers, e.g., clay, glass fibers, metal oxides, silica, and the like, can be used in 25 conventional amounts, preferably from 2 to 50 parts by weight per 100 parts by weight of the composition.

The present composition can also include impact modifiers, such as polystyrene resins which have been blended or co-polymerized with materials which are 30 elastomeric at room temperature, e.g., 20° to 25°C.



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The preferred styrene resins will be those having at least 25% by weight of repeating units derived from a vinyl aromatic compounds of the formula:



wherein R is hydrogen, (lower) alkyl or halogen;
Z is vinyl, halogen or (lower) alkyl; and p is 0 or
an integer of from 1 to the number of replaceable
hydrogen atoms on the benzene nucleus. Herein the
15 term "(lower) alkyl" means alkyl from 1 to 6 carbon
atoms.

The general formula above includes, by way of
illustration, homopolymers such as homopolystyrene
and monochloropolystyrene, the modified polystyrenes,
20 such as rubber modified high impact polystyrene, i.e.,
polystyrene which has been blended or grafted with
natural or synthetic elastomers such as poly-
butadiene, styrene-butadiene, EPDM rubber, and the
like, and styrene containing copolymers such as the
25 styrene acrylonitrile copolymers, styrene butadiene
copolymers, styrene acrylonitrile- α -alkyl styrene
copolymers, styrene-acrylonitrile-butadiene
copolymers, poly- α -methyl-styrene, copolymers of
ethylvinylbenzene, divinylbenzene and styrene maleic
30 anhydride copolymers, and block copolymers of
styrene-butadiene and styrene-butadiene styrene.
Preferred are rubber modified high impact
polystyrene resins.



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If an impact modifier is employed it should be used at about 3 to 15 parts by weight per 100 parts by weight of the composition.

The compositions can also include a flame retardant amount of a flame retardant agent. Obviously, the flame retardant agent can comprise plasticizer component (b) if (b) itself is a flame retardant and is present in flame retardant amounts, e.g., triphenyl phosphate in at least 10 parts by weight per 100 parts by weight of the total composition.

Other ingredients, such as pigments, stabilizers, lubricants, and the like may be added for their conventional purposes.

15 The manner in which the present compositions are prepared is not critical and conventional methods can be employed. Preferably, however, each of the ingredients is added as part of a blend premix, and the latter is passed through an extruder
20 at an extrusion temperature of from about 275 to about (340°F.) 171°C., dependent on the needs of the particular composition. The strands emerging from the extruder may be cooled, chopped into pellets, and molded or calendered to any desired shape.

25 Description of the Preferred Embodiments

The following example is illustrative of the composition of this invention. It is not intended to limit the invention in any manner.



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Example

The following compositions are prepared. All parts are by weight.

	<u>Composition I</u>	<u>Parts</u>
5	poly(2,6-dimethyl-1,4-phenylene) ether	100
	triphenyl phosphate	50

The powdered polyphenylene ether is placed in a Henschel mixer with the phosphate plasticizer and mixed until the powder temperature exceeds the phosphate melting temperature and the molten phosphate is absorbed by the polyphenylene ether.

	<u>Composition II</u>	<u>Parts</u>
15	poly(vinyl chloride) resin	54
	trio(2-ethylhexyl) tri-mellitate plasticizer	33
	Tribase Ex1	4
	#33 Clay (filler)	9

The resin is mixed with the plasticizer and filler in a Henschel mixer until the plasticizer is absorbed. One hundred parts of Composition I are dry mixed with 400 parts of Composition II and the blend is coextruded at (300°F.) 149°C. in a 28mm Werner-Pfleiderer twin screw extruder and chopped into pellets.

The pellets are injection-molded in a 3 oz. Newbury molding machine to produce test bars. The bars are subjected to standard tests and the following molded properties are obtained



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Tensile strength, (psi)kg/cm² (1700) 119
 Elongation, % 148
 Izod impact strength,
 (ft. lbs./in. notch)kg-cm (6.3) 34

5 The molded bars are flexible and show no visual signs of poly(vinyl chloride) degradation.

The bars are tested for flame retardance properties by the UL-94 test. The UL-94 test is generally carried out by preparing a molded test
 10 piece of about 13 cm x 1.3cm x 0.16 cm (5" x 1/2" x 1/16"), supporting the sample vertically, and igniting it. If the sample does not form flowing droplets sufficient to ingite a piece of cotton held 30.5 cm (12 inches) beneath and extinguishes
 15 itself within an average of 5 seconds after each of two 10-seconds ignitions, the composition is deemed to be non-dripping and flame-retardant to the point where it satisfies the V-0 requirements of the Underwriters' Laboratories. If the test sample
 20 extinguishes itself within 30 seconds, after two 10-second ignitions, the composition is deemed to be flame-retardant and non-dripping in satisfaction of the V-1 requirements.

	<u>Flame Out Times</u>				
	<u>UL - 94 (seconds)</u>				
25	3/1	5/7	1/3	1/13	2/33

It is seen that they are flame retardant.



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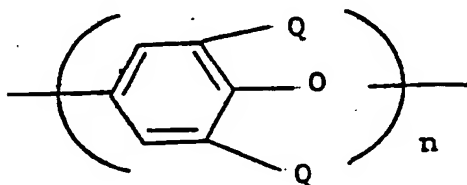
Obviously, other modifications and variations of the present invention are possible in the light of the above description. It is, therefore, to be understood that changes may be made in the particular embodiments disclosed herein which are within the full intended scope of the invention as defined in the appended claims.



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Claims

1. A thermoplastic composition which comprises,
in intimate admixture:
- (a) a polyphenylene ether resin;
 - (b) a plasticizer for component (a) in an
- 5 amount at least sufficient to reduce the
fusion temperature of (a) to below that at
which degradation of component (c) (i) or (c)
(ii) occurs; and (c) (i) a poly(vinyl chloride)
resin or (ii) a combination thereof with
- 10 a plasticizer therefor, the degradation
temperature of (c) (i) or (c) (ii) being at
least as high as the fusion temperature of
component (a) per se.
2. A composition as defined in claim 1 wherein the
- 15 polyphenylene ether resin (a) has the formula



20 wherein the oxygen ether atom of one unit is
connected to the benzene nucleus of the next
adjoining unit, n is a positive integer and is

25 at least 50, and each Q is a monovalent
substituent selected from the group consisting
of hydrogen, halogen, hydrocarbon radicals
free of a tertiary alpha-carbon atom, halo-

30 hydrocarbon radicals having at least two carbon
atoms between the halogen atom and the phenyl
nucleus, hydrocarbonoxy radicals and halohydro-

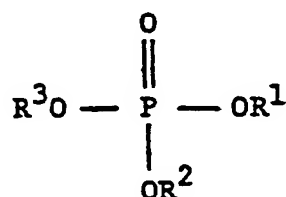


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carbonoxy radicals having at least two carbon atoms between the halogen atom and the phenyl nucleus.

3. A composition as defined in claim 2 wherein
5 the polyphenylene ether resin (a) is poly (2,6-dimethyl-1,4-phenylene) ether.
4. A composition as defined in claim 1 wherein the plasticizer (b) is a compound of the formula:

10



15

wherein R^1 , R^2 and R^3 are the same or different and are alkyl, cycloalkyl, aryl, alkyl substituted aryl, aryl substituted alkyl, hydroxyalkyl, hydroxyaryl, hydroxyalkaryl, halogen, haloaryl and hydrogen.

20

5. A composition as defined in claim 4 wherein said plasticizer (b) is an aromatic phosphate plasticizer.
6. A composition as defined in claim 5 wherein said aromatic phosphate is triphenylphosphate.
- 25 7. A composition as defined in claim 1 wherein the plasticizer component in (c) (ii) is an ester of an aromatic acid.
8. A composition as defined in claim 7 wherein the plasticizer in component (c) (ii) is
30 tri(2-ethylhexyl)trimellitate.



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9. A composition as defined in claim 1 which includes a filler.
10. A composition as defined in claim 1 wherein component (a) includes in combination therewith
5 a styrene resin.



INTERNATIONAL SEARCH REPORT

International Application No

PCT/US79/00370

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ¹		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int. Cl. C08K5/52	C08K5/12	
US Cl. 260/30.6R		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁴		
Classification System	Classification Symbols	
US	260/30.6R 260/899 260/31.8M	
Documentation Searched other than Minimum Documentation to the extent that such Documents are included in the Fields Searched ⁵		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ¹⁴		
Category ⁶	Citation of Document, ¹⁵ with indication, where appropriate, of the relevant passages ¹⁷	Relevant to Claim No. ¹⁸
X	US, A, 3,533,978, Published 13 October 1970, Bullman et al	1-10
X	US, A, 3,639,506, Published 01 February 1972, Haaf	1-10
X	US, A, 3,652,710, Published 28 March 1972, Holub et al	1-10
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IV. CERTIFICATION		
Date of the Actual Completion of the International Search ¹		Date of Mailing of this International Search Report ²
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International Searching Authority ¹		Signature of Authorized Officer ²⁰
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